

# Pulse NMR Study of Glass Transition in Maltodextrin

R. Ruan, Z. Long, P. Chen, V. Huang, S. Almaer, and I. Taub

## ABSTRACT

A pulse nuclear magnetic resonance (NMR) technique was used to study the glass transition in maltodextrins. The spin-lattice relaxation time ( $T_1$ ) and spin-spin relaxation time ( $T_2$ ) of different molecular weight maltodextrins at different moisture contents and temperatures were measured using the pulse NMR technique.  $T_1$  and  $T_2$  were plotted against temperatures. From the resultant curves, the state transitions were observed and the corresponding state transition temperatures were determined. The state transition temperatures were very close to the glass transition temperatures ( $T_g$ s) determined with differential scanning calorimetry, suggesting a strong relationship between glass transition and proton relaxation behavior. Results indicate pulse NMR-based instrumentation could be very effective for the study of glass transition in food polymers.

**Key Words:** DSC, glass transition, maltodextrin, NMR, relaxation time

## INTRODUCTION

THE PHYSICAL PROPERTIES OF AMORPHOUS FOOD MATERIALS CAN be related to the glass transition temperature ( $T_g$ ), a state change temperature at which the material glassy state is transformed to the rubbery state. The result of this state transition is molecular mobility, elasticity and solution viscosity. These properties govern time-dependent, viscosity-related structural transformations such as stickiness, elasticity, collapse and crystallization during processing and storage. Such transformations are of great importance to the quality and stability of food products.

Most published  $T_g$  data of food materials were obtained using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and dynamic mechanical thermal analysis (DMTA) (Roos and Karel, 1990, 1991; Lambelet et al., 1991; Kalichevsky et al., 1992ab), which measure thermal or thermomechanical characteristics accompanying the transitions. However, these methods are limited to specific forms and sizes of the test specimens. For example, DSC uses a very small specimen (around 5–20 mg), which may not be reliably representative with reference to inhomogeneous food products. DMA and DMTA require a shapeable solid sample, and are thus not applicable for measurements on powder and semi-solid samples. Loss of moisture from the specimen into its large sample chamber during testing is another deficiency of DMTA. Difficulties in identifying  $T_g$ s from the DSC, DMA and DMTA data have also been reported with food materials.

Pulse nuclear magnetic resonance (NMR) has been reported as an

alternative method for the study of glass transition. NMR is a spectroscopic technique based on the magnetic properties of atomic nuclei, and is often used to monitor motional properties of molecules by analyzing the relaxation characteristics of the NMR active nuclei, such as  $^1\text{H}$  and  $^{17}\text{O}$ . The fact that molecular motions are fundamental to the glass transition of polymers (Perez, 1994) suggests that NMR may have a strong potential in the study of the glass transition. Kalichevsky et al. (1992a, b; 1993) and Ablett et al. (1993) using NMR, studied the spin-spin relaxation characteristics during the glass transition in several carbohydrates and proteins. They found that the behavior of the spin-spin relaxation time ( $T_2$ ) of the “rigid” component was related to the glass transition. More experiments on a wider spectrum of materials and a better understanding of the techniques are needed to verify the applicability of this methodology. In addition, few studies have been reported on the changes in the spin-lattice relaxation time ( $T_1$ ) in food polymers during the glass transition.

Our objective was to develop and test a pulse NMR based system for analysis of the glass transition processes in food products.

## MATERIALS & METHODS

### Sample preparation

Amorphous maltodextrin powders with DEs of 5, 15 and 25 and theoretical molecular weights (MW) of 3600, 1200 and 720, respectively (Grain Processing Corporation, Muscatine, IA) were used. To obtain well mixed samples, a cold mixing procedure similar to that described by Kalichevsky et al. (1992a) was employed. A known amount of distilled water was sprinkled into liquid nitrogen in a mortar to form ice crystals, which were ground with a pestle to fine ice powder. Liquid nitrogen and appropriate weights of maltodextrin were added to the mortar and mixed to provide a uniform mixture of powdered ice and maltodextrin, which was stored in a freezer for later use. The mixture was put in a refrigerator for at least 24h to facilitate even distribution of water before measurement. Moisture contents of the samples were determined by drying at 70°C for 24h. Test samples were placed into glass test tubes (12mm dia., for NMR experiments) or aluminum pans (TA Instruments, 60  $\mu\text{L}$ , for DSC experiments), sealed and allowed to equilibrate at room temperature ( $\sim 23^\circ\text{C}$ ) for 2h prior to measurement.

### NMR relaxation measurement

A 20MHz PCT 20/30 NMR Analyzer (Process Control Technology, Inc., Denver, CO) was used. The analyzer was equipped with a temperature control system developed in Department of Biosystems and Agricultural Engineering, Univ. of Minnesota. The temperature-control system consisted of a Barber-Colman 560 series temperature controller, a Luxtron 750 fiber-optic, nonmagnetic temperature sensor, an electric heater, a liquid nitrogen container, and a nitrogen gas cylinder. The fiber-optic temperature sensor was inserted into the center of the sample to monitor the real-time temperature of the sample. Designated temperatures were maintained by automatic adjustment of the amount of heating and cooling that the samples received. Temperature calibration of the system was carried out using real samples. The calibration result was used only as a guideline for adjusting the heating and cooling devices to achieve a target temperature at a desired rate.

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For each test, a maltodextrin sample (about 2.5g) was placed in a glass test tube of 12 mm dia. The 90° NMR pulse sequence and T1SR ( $T_1$  saturation recovery) pulse sequence were used to measure the spin-spin relaxation time and spin-lattice relaxation time. A 90° pulse of 15  $\mu$ s was applied to the sample. The sequence repetition time was set to 1s. The dwell time between data was 0.5  $\mu$ s. The number of data points acquired in the 90° pulse experiment and the T1SR experiment were 320 and 16, respectively. Sixteen scans were accumulated to increase the signal to noise ratio. The temperature range in the NMR experiments was  $\pm 50^\circ\text{C}$  around the expected  $T_g$  of the samples used. Each sample was measured at eight temperature points. At every point, the sample was allowed to equilibrate for 5 min before measurement. The temperature of the sample was recorded using the fiber optic probe with an accuracy of  $\pm 0.1^\circ\text{C}$ .

### DSC experiment

The DSC measurement was made on a UNIX DSC 7 (The Perkin-Elmer Corporation, Norwalk, CT), calibrated by daily measurement of the melting point of pure indium. Samples (15 mg) were weighed into an aluminum pan and sealed, cooled to  $-80^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$  and then heated to  $80^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ .  $T_g$  (the mid point) was calculated using the built-in computer program within the DSC system.

### Statistical analysis

One-way and two-way ANOVAs with duplication were used to analyze the effects of moisture content, number of DEs, and methods ( $T_1$ ,  $T_2$  and DSC) on glass transition measurements. The ANOVA program was part of *Microsoft Excel 97* (Microsoft Corp., Seattle, WA).

## RESULTS & DISCUSSION

THE FREE INDUCTION DECAY (FID) CURVE FROM THE ONE-PULSE test (Fig. 1) showed that two components of protons with different relaxation rates existed in the sample, which could be identified by applying the bi-Gaussian function:

$$M = M_s \times \exp(-t^2/T_{2s}^2) + M_M \times \exp(-t^2/T_{2M}^2)$$

where  $M$  is the NMR signal intensity at time  $t$ ,  $T_{2s}$  and  $T_{2M}$  were the spin-spin relaxation times corresponding to the "rigid" and "more mobile" protons,  $M_s$  and  $M_M$  were proportional to the numbers of protons in the  $T_{2s}$  and  $T_{2M}$  states, respectively. Since no  $180^\circ$  refocus pulse was used in the experiments, the spin-spin relaxation time constants are apparent relaxation time constants, i.e.,  $T_{2s}^*$  and  $T_{2M}^*$ .

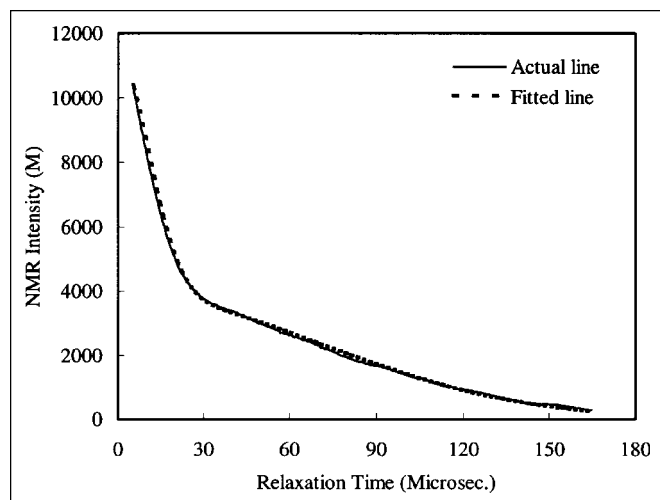
However, for solid samples (like ours), the intrinsic  $T_2$  was very close to the  $T_2^*$  (Fullerton and Cameron, 1988). Therefore,  $T_{2s}$  was used for convenience.

$T_{2s}$  is hypothesized to be associated with the relaxation behavior of carbohydrate protons. Thus,  $T_{2s}$  provides crucial information on the molecular structure and mobility of the carbohydrates. Kalichevsky et al. (1992b), in their study of  $T_g$  of amylopectin, gluten, gluten-sugar mixtures with NMR, related  $T_{2s}$  to the "rigid lattice limit temperature ( $T_{RLL}$ )", which they hypothesized was closely associated with glass transition changes in the samples. They reported that  $T_{2s}$  increased rapidly with temperature after passing a transition point,  $T_{RLL}$ .

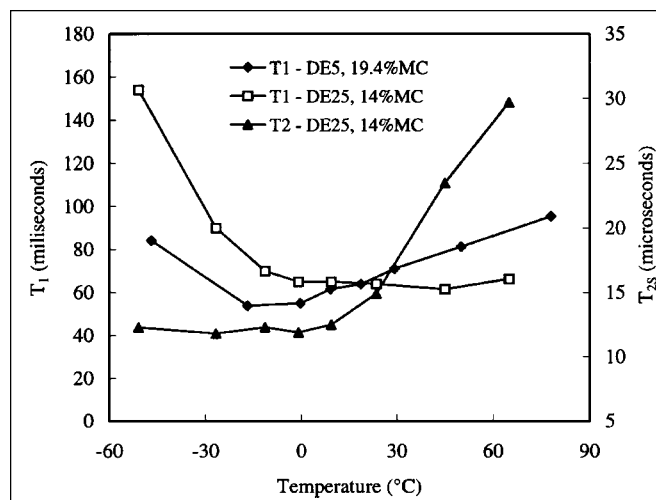
Representative plots of relaxation time vs temperature in this study showed that  $T_{2s}$  was almost constant or increased very slowly with increasing temperature when below a certain temperature. Then  $T_{2s}$  increased more rapidly after passing that temperature point (Fig. 2,  $T_2$ -DE25, 14%MC). All the  $T_{2s}$ -temperature curves were characterized by a mirrored "L" shape. However,  $T_1$  behaved in an opposite way in the case of DE15 and DE25, and the  $T_1$ -temperature curves were characterized by an "L" shape (Fig. 2,  $T_1$ -DE25, 14%MC). In the case of DE5,  $T_1$  increased after passing the lowest point, and U-shape curves were obtained (Fig. 2,  $T_1$ -DE5, 19.4%).

The turning points on the curves (Fig. 2) may indicate the state transitions in the samples as temperature changed, and were therefore of great interest. The turning points were determined from a mirrored "L"-shaped curve (Fig. 3). The curve had two nearly linear phases with different slopes. The point where the two lines meet was regarded as a turning point and the corresponding temperature was recorded as the state transition temperature. For the "U"-shaped curves, the lowest points were taken as the turning points and the corresponding temperatures as state transition temperatures. A computer program was written to make the determinations of these state transition temperatures.

To evaluate the relationships between the proton relaxation behaviors and glass transition phenomena in maltodextrins, the state transition temperature and  $T_g$  were plotted vs moisture content for DE5 (Fig. 4), DE15 (Fig. 5) and DE25 (Fig. 6).  $T_g$  decreased with increasing moisture content due to the increased plasticization effect of water in the sample. State transition temperatures determined by NMR methods followed the same trend. At each moisture level, the state transition temperature approximated the  $T_g$ . In general, the state transition temperatures determined from  $T_{2s}$ -temperature curves were closer to the  $T_g$  than were those determined from  $T_1$ -temperature curves. The



**Fig. 1—Example of spin-spin relaxation curve demonstrating that the data are well fitted by a bi-Gaussian equation.**



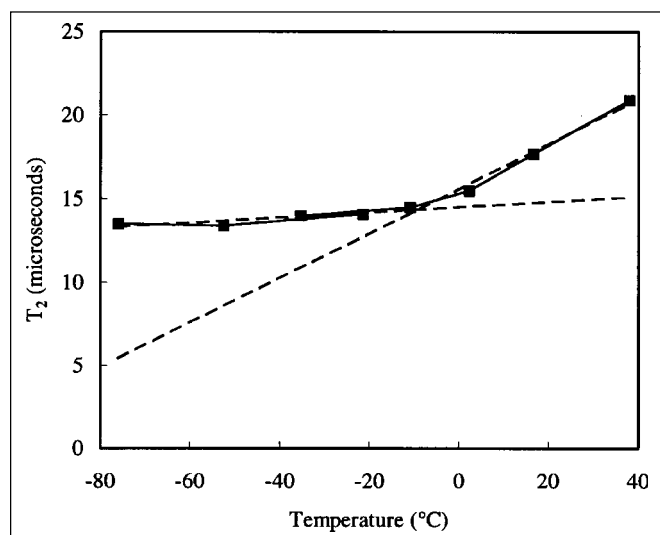
**Fig. 2—Representative plots of relaxation time vs temperature. %MC indicates the moisture contents (dry basis) of the samples.**

$T_{2s}$ -determined  $T_g$ s were generally higher and the  $T_1$ -determined  $T_g$ s lower than the  $T_g$ s determined by DSC. Note that both the state transition temperature and  $T_g$  decreased with increasing DE (or decreasing molecular weight) and increasing moisture content of maltodextrins, a typical behavior of polymers. Moisture content and DE had significant effects on glass transition temperature ( $p \leq 0.05$ ), and differences between  $T_{2s}$  and DSC results were not significant ( $P > 0.01$ ).

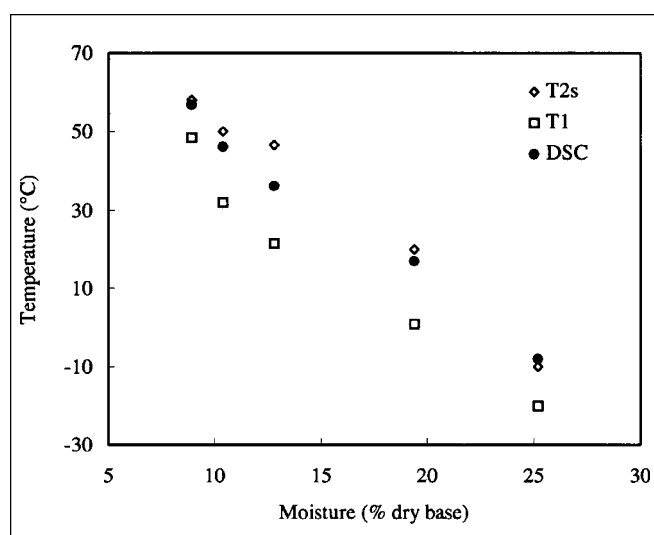
In general, a change in  $T_{2s}$  as affected by temperature is associated with the thermal motion of molecules. However, when the material enters the rubbery state (above  $T_g$ ), such motion is intensified due to the increased molecular mobility of the pendants and segments of the molecules. Thus after passing the state transition temperature, the mobility of protons connected with the carbons of the pendants and segments increases sharply with temperature as indicated by a much steeper slope on the  $T_{2s}$ -temperature curves. This agrees with results observed in the specific volume change in materials undergoing glass

transition.

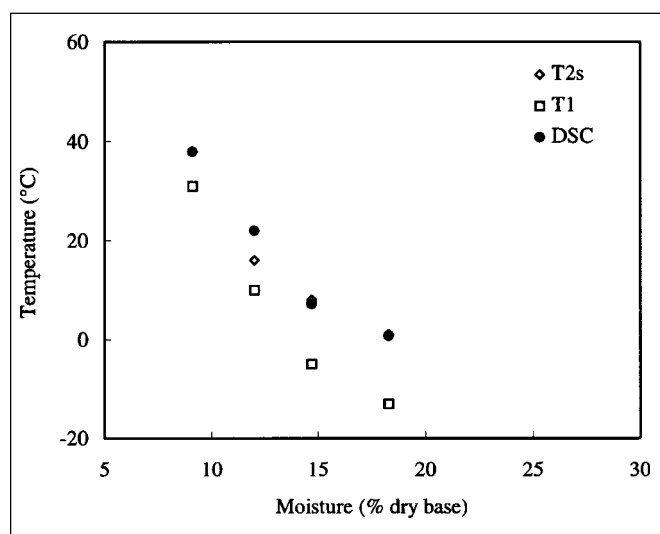
An increase in  $T_1$  with decreasing temperature below the state transition temperature or  $T_g$  is probably due to the material losing its ability to undergo segmental motion in the glassy state, or the segmental mobility of the material became "frozen" (Perepechko, 1980). The material could be treated as a solid in the glassy state where most of the proton and other segmental rotation occurs at a frequency lower than the resonance frequency, and requires a much longer correlation time. Because the number of protons and segments rotating at the resonance frequency is small, the dynamic contribution to  $T_1$  is very small, resulting in an inefficient  $T_1$  relaxation and a very long spin-lattice relaxation time at low temperature (Fullerton and Cameron, 1988). As the temperature increased and approached  $T_g$ , the number of protons and segments rotating at the resonance frequency increased. More protons and segments could then participate in the spin-lattice relaxation process, gradually decreasing  $T_1$ . As temperature increased above



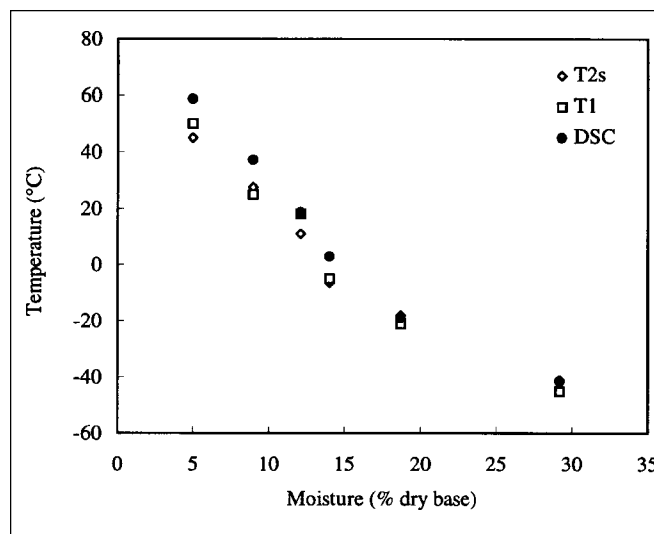
**Fig. 3—Determination of turning point on a mirrored "L"-shaped curve.**



**Fig. 4— $T_g$  determined by DSC and phase transition temperatures determined using  $T_{2s}$ - and  $T_1$ -temperature relationships as a function of moisture content in DE5 maltodextrin.**



**Fig. 5— $T_g$  determined by DSC and phase transition temperatures determined using  $T_{2s}$ - and  $T_1$ -temperature relationships as a function of moisture content in DE15 maltodextrin.**



**Fig. 6— $T_g$  determined by DSC and phase transition temperatures determined using  $T_{2s}$ - and  $T_1$ -temperature relationships as a function of moisture content in DE25 maltodextrin.**

the  $T_g$ , the structure transformed from rigid to soft, and became more flexible. For DE5, after a broad transition phase (viscous phase),  $T_1$  increased with temperature as it mainly depended upon the thermal motion of the molecules in the rubbery state or "liquid" phase. For DE15 and DE25, no significant increase in  $T_1$  as temperature increased, or a  $T_1$  minimum, was observed, although it might have occurred if a wider temperature range had been used. Although minimum  $T_1$  is also equipment dependent or, more precisely, frequency dependent (Fullerton and Cameron, 1988), this dependence would be much smaller than that on the composition and glass transition (Ruan and Chen, 1998).

## CONCLUSIONS

THE  $T_1$ - AND  $T_{2S}$ -TEMPERATURE CURVES OBTAINED WITH THE pulse NMR techniques showed that there were state transition points around the  $T_g$  values determined by DSC. The temperature-dependence of the proton spin-spin relaxation was insignificant when temperature was lower than the glass transition temperature, but increase significantly above  $T_g$ . For spin-lattice relaxation, the relaxation times decreased with temperatures below  $T_g$ , but decreased with temperature above  $T_g$ . Results demonstrated that the state transition temperature of a maltodextrin sample could be determined from the relaxation time-temperature curve, which approximated the glass transition temperature of the sample. The results suggest that pulse NMR based instrumentation could be used effectively in the study of glass transition phenomena in food polymers.

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